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Crystal structure of monocarbonyl[2-((cyclopentylmethylene)amino)-5-methylphenolato- κ^2 N,O] (tricyclohexylphosphine)rhodium(I), $C_{32}H_{48}NO_2PRh$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.31 × 0.30 × 0.28 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.65 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, ω
$\theta_{\max}$, completeness:	28.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	56087, 7280, 0.076
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6798
$N(\text{param})_{\text{refined}}$:	336
Programs:	SHELX [1], Bruker [2], Diamond [3], Olex2 [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Rh1	0.40316(2)	0.82694(4)	0.61162(3)	0.03373(10)
P1	0.37808(4)	0.67007(16)	0.48008(9)	0.0304(2)
O1	0.47277(13)	0.7938(4)	0.5524(3)	0.0479(10)
O2	0.29663(17)	0.8552(8)	0.6634(5)	0.097(2)
N1	0.43465(15)	0.9765(5)	0.7250(3)	0.0349(9)
C1	0.51311(18)	0.8757(5)	0.5652(4)	0.0340(10)
C2	0.55303(19)	0.8580(6)	0.4928(4)	0.0412(12)
H2	0.549356	0.787056	0.437360	0.049*
C3	0.5965(2)	0.9386(5)	0.4995(4)	0.0435(11)
C4	0.6369(2)	0.9251(8)	0.4184(5)	0.0572(16)
H4A	0.666947	0.881958	0.450690	0.086*
H4B	0.644657	1.025489	0.390196	0.086*
H4C	0.625586	0.858916	0.361590	0.086*
C5	0.6024(2)	1.0380(6)	0.5850(5)	0.0480(13)
H5	0.632771	1.092501	0.592951	0.058*
C6	0.5650(2)	1.0569(6)	0.6564(5)	0.0439(12)
H6	0.570075	1.123937	0.713593	0.053*
C7	0.51905(18)	0.9796(5)	0.6478(4)	0.0352(10)
C8	0.48107(19)	1.0178(6)	0.7224(4)	0.0380(11)
H8	0.491369	1.082570	0.777705	0.046*
C9	0.4053(2)	1.0490(6)	0.8078(4)	0.0432(11)
H9	0.429241	1.105901	0.853202	0.052*
C10	0.3753(2)	0.9435(7)	0.8796(5)	0.0548(14)
H10A	0.359296	0.861047	0.839314	0.066*
H10B	0.396714	0.899099	0.934919	0.066*
C11	0.3368(3)	1.0500(10)	0.9257(7)	0.087(3)
H11A	0.306434	0.993237	0.945553	0.105*
H11B	0.350370	1.099817	0.989103	0.105*
C12	0.3248(2)	1.1640(9)	0.8456(5)	0.0662(17)

<https://doi.org/10.1515/ncrs-2020-0248>

Received May 21, 2020; accepted June 2, 2020; available online June 18, 2020

Abstract

$C_{32}H_{48}NO_2PRh$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 26.784(10)$ Å, $b = 8.837(3)$ Å, $c = 12.759(4)$ Å, $V = 3020.0(18)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0400$, $wR_{\text{ref}}(F^2) = 0.0920$, $T = 100(2)$ K.

CCDC no.: 2007109

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H12A	0.321520	1.265107	0.878223	0.079*
H12B	0.292797	1.138495	0.810889	0.079*
C13	0.3673(2)	1.1642(7)	0.7655(5)	0.0534(13)
H13A	0.382456	1.266033	0.759944	0.064*
H13B	0.354965	1.133358	0.695483	0.064*
C14	0.3387(2)	0.8448(8)	0.6469(5)	0.0561(15)
C21	0.3648(2)	0.7756(6)	0.3592(4)	0.0425(12)
H21	0.355303	0.700647	0.303999	0.051*
C22	0.3207(2)	0.8817(7)	0.3748(6)	0.0563(15)
H22A	0.328530	0.953599	0.431993	0.068*
H22B	0.291158	0.822069	0.396150	0.068*
C23	0.3084(3)	0.9702(9)	0.2758(6)	0.076(2)
H23A	0.281130	1.042726	0.290492	0.091*
H23B	0.296804	0.899677	0.220581	0.091*
C24	0.3546(4)	1.0561(10)	0.2370(7)	0.094(3)
H24A	0.346675	1.107201	0.169933	0.113*
H24B	0.363738	1.134776	0.288766	0.113*
C25	0.3976(4)	0.9513(10)	0.2214(7)	0.095(3)
H25A	0.427206	1.010646	0.199635	0.114*
H25B	0.389575	0.879592	0.164246	0.114*
C26	0.4102(3)	0.8629(8)	0.3197(5)	0.0647(18)
H26A	0.421752	0.933413	0.374882	0.078*
H26B	0.437621	0.791129	0.304530	0.078*
C31	0.42584(19)	0.5300(6)	0.4472(4)	0.0391(11)
H31	0.455338	0.597257	0.435364	0.047*
C32	0.4242(3)	0.4501(10)	0.3496(6)	0.084(3)
H32A	0.424062	0.525508	0.292222	0.101*
H32B	0.392193	0.394366	0.346077	0.101*
C33	0.4644(3)	0.3435(10)	0.3300(7)	0.083(2)
H33A	0.452762	0.270185	0.276660	0.100*
H33B	0.492703	0.400030	0.298929	0.100*
C34	0.4830(3)	0.2592(10)	0.4187(9)	0.096(3)
H34A	0.462335	0.167136	0.426879	0.115*
H34B	0.517473	0.225871	0.402702	0.115*
C35	0.4837(3)	0.3374(10)	0.5167(7)	0.082(2)
H35A	0.515463	0.394301	0.521407	0.098*
H35B	0.483876	0.261075	0.573423	0.098*
C36	0.4431(2)	0.4422(7)	0.5366(5)	0.0477(13)
H36A	0.453804	0.513475	0.592100	0.057*
H36B	0.414402	0.384042	0.564540	0.057*
C18	0.2499(3)	0.3206(10)	0.5277(7)	0.082(2)
H18A	0.213609	0.314154	0.541944	0.099*
H18B	0.262517	0.215517	0.522842	0.099*
C15	0.32237(14)	0.5514(5)	0.4993(4)	0.0391(11)
H15	0.297576	0.634778	0.509360	0.047*
C20	0.2991(2)	0.4803(7)	0.4108(6)	0.0610(17)
H20A	0.289996	0.560985	0.360515	0.073*
H20B	0.324634	0.416364	0.376227	0.073*
C17	0.2727(3)	0.3890(8)	0.6156(7)	0.071(2)
H17A	0.281689	0.307582	0.665424	0.086*
H17B	0.247307	0.453005	0.650432	0.086*
C16	0.3167(2)	0.4810(8)	0.5990(5)	0.0607(16)
H16A	0.316993	0.561435	0.653024	0.073*
H16B	0.346385	0.416648	0.611330	0.073*
C19	0.2561(2)	0.3892(8)	0.4273(6)	0.0672(19)
H19A	0.256255	0.307682	0.374058	0.081*
H19B	0.226306	0.452679	0.413508	0.081*

Source of material

A solution of the [Rh(5-Me-Sal-CyPent)(CO)₂], was obtained from the addition of 2-(cyclopentyl)methyl-5-methylphenol (5-Me-Sal-CyPent), to a DMF solution of tetracarbonyl-dichloro-dirhodium(I). The title compound was obtained by the addition of tricyclohexylphosphine (PCy₃) to the dicarbonyl precursor. Suitable crystals were obtained upon evaporation of the acetone solution at room temperature.

Experimental details

H-atoms were positioned on geometrically idealized positions and refined using the riding model with fixed C—H distances for aromatic C—H of 0.93 Å (C—H) [*U*_{iso} (H) = 1.2 *U*_{eq}], for methyl C—H of 0.96 Å (C—H) [*U*_{iso} (H) = 1.5 *U*_{eq}], for methylene C—H of 0.97 Å (C—H) [*U*_{iso} (H) = 1.5 *U*_{eq}] and for methine C—H of 0.98 Å (C—H) [*U*_{iso} (H) = 1.5 *U*_{eq}]. The graphics were obtained using the DIAMOND [3] program with 50% probability ellipsoids. The highest residual peak is located 0.22 Å from H22B and the deepest hole is situated −0.41 Å from H16B.

Comment

The rhodium(I) square planar complexes of the type [Rh(L,L-Bid)(CO)(PR₃)], where L,L-Bid = monoanionic bidentate ligands and PR₃ represents the tertiary phosphine ligands, have been investigated extensively as potential catalyst precursors [5–11]. These [Rh(L,L'-Bid)(CO)(PR₃)] complexes are in general easily obtained from the substitution of one carbonyl ligand in the parent complex Rh(L,L'-Bid)(CO)₂, by monodentate tertiary phosphines. Previous studies have indicated that the substitution of one carbonyl ligand from the parent dicarbonyl complex may lead to the formation of two isomers with preference given to the stronger donor atom when there is a pronounced difference in the nature of the donating and accepting properties between the donor atoms L and L'. If the donor atoms have comparable donor capabilities, the isomers form in comparable ratio [12, 13].

A perspective diagram of the title compound indicates that the phosphine ligand is *trans* to the nitrogen atom of the Schiff-base ligand in accordance with the relative *trans* influence of S > N > O atoms [14–17]. The electronegativity of these donor atoms is not the sole directing factor in the substitution reaction as was indicated in previous studies, that there is competition between the electronic and steric parameters [18–20].

The central rhodium atom in the title compound is coordinated to a carbonyl ligand, the bulky PCy₃ ligand and the nitrogen and oxygen atoms of the bidentate chelate ligand forming a square planar geometry. The square planar orientation around the rhodium atom is distorted from the ideal geometry as indicated by the O1—Rh—N1 bite angle of 89.03(18)° and the C14—Rh—O2 angle of 171.7(2)°. The

rhodium central atom is displaced by 0.0351(3) Å from the plane constructed through O1–N1–C14–P1. The Rh–N and Rh–O bond lengths 2.1365(4) Å and 2.0360(6) Å are in good agreement to those found in other rhodium(I) complexes with N,O donor atoms with bond distances spanning around 2.077–2.092 Å and 2.018–2.036 Å for Rh–N and Rh–O respectively [21–23].

Acknowledgements: We would like to thank the University of the Free State for Financial assistance. We also express our gratitude towards SASOL, Gerdus Kemp and PETLabs Pharmaceuticals, the South African National Research Foundation (SA-NRF) for financial support of this project.

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